

# PATENT COOPERATION TREATY

**PCT**

## NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

MOENS, Marnix, Karel, Christiane  
Huntsman ICI Europe Ltd  
Huntsman Polyurethanes  
Intellectual Property Dept.  
Everslaan 45  
B-3078 Everberg  
BELGIQUE

|   |  |
|---|--|
| <b>Date of mailing (day/month/year)</b><br>22 March 2001 (22.03.01) |  |
| <b>Applicant's or agent's file reference</b><br>EUR 50799/WO        | <b>IMPORTANT NOTIFICATION</b>  |
| <b>International application No.</b><br>PCT/EP00/06057              | <b>International filing date (day/month/year)</b><br>29 June 2000 (29.06.00) |

|  |                                   |                                 |
|--|-----------------------------------|---------------------------------|
| <b>1. The following indications appeared on record concerning:</b><br><input checked="" type="checkbox"/> the applicant <input type="checkbox"/> the inventor <input type="checkbox"/> the agent <input type="checkbox"/> the common representative  |                                   |                                 |
| <b>Name and Address</b><br>HUNTSMAN ICI CHEMICALS, LLC<br>500 Huntsman Way<br>Salt Lake City, UT 84108<br>United States of America   | <b>State of Nationality</b><br>US | <b>State of Residence</b><br>US |
|  | <b>Telephone No.</b>              |                                 |
|  | <b>Facsimile No.</b>              |                                 |
|  | <b>Teleprinter No.</b>            |                                 |
| <b>2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:</b><br><input type="checkbox"/> the person <input checked="" type="checkbox"/> the name <input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence  |                                   |                                 |
| <b>Name and Address</b><br>HUNTSMAN INTERNATIONAL LLC<br>500 Huntsman Way<br>Salt Lake City, UT 84108<br>United States of America  | <b>State of Nationality</b><br>US | <b>State of Residence</b><br>US |
|  | <b>Telephone No.</b>              |                                 |
|  | <b>Facsimile No.</b>              |                                 |
|  | <b>Teleprinter No.</b>            |                                 |
| <b>3. Further observations, if necessary:</b>  |                                   |                                 |
| <b>4. A copy of this notification has been sent to:</b><br><div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> the receiving Office<br/> <input checked="" type="checkbox"/> the International Searching Authority<br/> <input type="checkbox"/> the International Preliminary Examining Authority                         </div> <div> <input checked="" type="checkbox"/> the designated Offices concerned<br/> <input type="checkbox"/> the elected Offices concerned<br/> <input type="checkbox"/> other:                         </div> </div> |                                   |                                 |

|  |   |
|--|---|
| <b>The International Bureau of WIPO</b><br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland<br><br>Facsimile No.: (41-22) 740.14.35 | <b>Authorized officer</b><br><br>Dominique DELMAS<br><br>Telephone No.: (41-22) 338.83.38 |
|--|---|



# PATENT COOPERATION TREATY



## PCT

### NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
US Department of Commerce  
United States Patent and Trademark  
Office, PCT  
2011 South Clark Place Room  
CP2/5C24  
Arlington, VA 22202  
ETATS-UNIS D'AMERIQUE  
in its capacity as elected Office

|  |  |
|--|--|
| <b>Date of mailing</b> (day/month/year)<br>06 April 2001 (06.04.01)          |  |
| <b>International application No.</b><br>PCT/EP00/06057                       | <b>Applicant's or agent's file reference</b><br>EUR 50799/WO     |
| <b>International filing date</b> (day/month/year)<br>29 June 2000 (29.06.00) | <b>Priority date</b> (day/month/year)<br>26 July 1999 (26.07.99) |
| <b>Applicant</b><br>SKINNER, Christopher, John                               |  |

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

08 February 2001 (08.02.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

|   |  |
|---|--|
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland<br>Facsimile No.: (41-22) 740.14.35 | Authorized officer<br>S. Mafla<br>Telephone No.: (41-22) 338.83.38 |
|---|--|

# PATENT COOPERATION TREATY

## PCT

REC'D 26 OCT 2001

D PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

|  |   |   |   |
|--|---|---|---|
| Applicant's or agent's file reference<br><b>EUR 50799/WO</b>                                     | <b>FOR FURTHER ACTION</b>                                       |   | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
| International application No.<br><b>PCT/EP00/06057</b>   | International filing date (day/month/year)<br><b>29/06/2000</b> | Priority date (day/month/year)<br><b>26/07/1999</b> |   |
| International Patent Classification (IPC) or national classification and IPC<br><b>C08G18/22</b> |   |   |   |
| Applicant<br><b>HUNTSMAN INTERNATIONAL LLC et al.</b>  |   |   |   |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
  
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 

☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of    sheets.

3. This report contains indications relating to the following items:

- I    ☒ Basis of the report
- II    ☐ Priority
- III    ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV    ☐ Lack of unity of invention
- V    ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI    ☐ Certain documents cited
- VII    ☐ Certain defects in the international application
- VIII    ☐ Certain observations on the international application

|   |  |
|---|--|
| Date of submission of the demand<br><br><b>08/02/2001</b>   | Date of completion of this report<br><br><b>24.10.2001</b>                     |
| Name and mailing address of the international preliminary examining authority:<br><br>European Patent Office<br>D-80298 Munich<br>Tel. +49 89 2399 - 0 Tx: 523656 epmu d<br>Fax: +49 89 2399 - 4465 | Authorized officer<br><br><b>West, N</b><br><br>Telephone No. +49 89 2399 7582 |



INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

International application No. PCT/EP00/06057

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-13 as originally filed

**Claims, No.:**

1-23 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/06057

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

|                               |      |        |                |
|-------------------------------|------|--------|----------------|
| Novelty (N)                   | Yes: | Claims |                |
|                               | No:  | Claims | 1,8,20,23      |
| Inventive step (IS)           | Yes: | Claims |                |
|                               | No:  | Claims | 2-7,9-19,21-22 |
| Industrial applicability (IA) | Yes: | Claims | 1-23           |
|                               | No:  | Claims |                |

2. Citations and explanations  
**see separate sheet**

Reference is made to the following documents (**D**):

**D1:** WO 97 17388 A (ICI PLC) 15 May 1997 (1997-05-15)

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Document **D1** discloses a polyisocyanate composition comprising a titanium complex, consisting of titanium and an acetoacetate ester in which the molar ratio of titanium to acetoacetate ester is 1:2 and said acetoacetate ester is an ester of an alcohol having 1 to 30 carbon atoms (p. 2, lines 1-14; p. 2, line 40-p. 3, line 13). The titanium complex is used in amounts varying between 0.1 and 10% by weight based on the polyisocyanate (claim 14).

**D1** also discloses the use of conventional release agents, which can be added to the polyisocyanate composition. These are used in an amount varying between 0.2 and 10% by weight based on the polyisocyanate (p. 6, lines 35-42).

Document **D1** furthermore discloses a process for binding lignocellulosic material comprising the steps of (a) bringing lignocellulosic material into contact with a polyisocyanate composition falling into the scope of the present application and (b) allowing said material to bind (p. 13, lines 23-31). The combination of the polyisocyanate composition and the lignocellulosic material is performed by hot-pressing at 150°C to 250°C and 2 to 6 MPa (p. 13, lines 33-39). The polyisocyanate compositions are applied in amounts to give a weight ratio of polyisocyanate/lignocellulosic material in the range of 1:99.9 to 20:80 (p. 14, lines 27-32).

It is inherently known from **D1** that the titanium complexes are used as catalysts for accelerating the binding of lignocellulosic materials.

As a consequence, claims 1,8,20 and 23 of the present application lack novelty, i.e. are not in accordance with Article 33(2) PCT.



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP00/06057

Due to the severe novelty objections, the subject-matter of the remaining claims are for person skilled in the art merely routine variations. Therefore, the subject-matter of claims 2-7, 9-19 and 21-22 lack inventive step (Article 33(3) PCT).

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|  |  |  |
|--|--|--|
| Applicant's or agent's file reference<br><b>EUR 50799/WO</b> | <b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small> |  |
| International application No.<br><b>PCT/EP 00/ 06057</b>     | International filing date (day/month/year)<br><b>29/06/2000</b>  | (Earliest) Priority Date (day/month/year)<br><b>26/07/1999</b> |
| Applicant<br><br><b>HUNTSMAN ICI CHEMICALS LLC</b>           |  |  |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of Invention is lacking** (see Box II).

**4. With regard to the title,**

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established by this Authority to read as follows:

**5. With regard to the abstract,**

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

**6. The figure of the drawings to be published with the abstract is Figure No.**

- ☐ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.
- ☐ None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No

P 00/06057

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C08G18/22 C08G18/76

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.       |
|------------|---|-----------------------------|
| X          | WO 97 17388 A (ICI PLC)<br>15 May 1997 (1997-05-15)<br><br>claims 1,4,5,15,32-35,39,43,44; example 2<br>---   | 1,2,5-7,<br>10-16,<br>20-23 |
| A          | US 5 902 835 A (KIMOCK MICHAEL JOHN ET AL)<br>11 May 1999 (1999-05-11)<br>column 2, line 52 -column 3, line 14;<br>claims 1,2<br>---  | 1,4-10,<br>13               |
| A          | DATABASE WPI<br>Section Ch, Week 197746<br>Derwent Publications Ltd., London, GB;<br>Class A21, AN 1977-82339Y<br>XP002115290<br>& JP 50 138097 A (HITACHI LTD),<br>4 November 1975 (1975-11-04)<br>abstract<br>----- | 1,5-7,<br>11,13             |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 September 2000

Date of mailing of the international search report

04/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Angiolini, D

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P EP 00/06057

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---|---------------------|----------------------------|---------------------|
| WO 9717388                                | A | 15-05-1997          | AU 7298096 A               | 29-05-1997          |
|   |   |                     | BR 9611385 A               | 26-01-1999          |
|   |   |                     | CN 1201469 A               | 09-12-1998          |
|   |   |                     | CZ 9801369 A               | 12-08-1998          |
|   |   |                     | EP 0859805 A               | 26-08-1998          |
|   |   |                     | JP 11514690 T              | 14-12-1999          |
|   |   |                     | NO 982043 A                | 06-07-1998          |
|   |   |                     | PL 326551 A                | 28-09-1998          |
|   |   |                     | SK 59098 A                 | 09-09-1998          |
| US 5902835                                | A | 11-05-1999          | BR 9901754 A               | 11-04-2000          |
|   |   |                     | EP 0960894 A               | 01-12-1999          |
|   |   |                     | JP 2000026564 A            | 25-01-2000          |
| JP 50138097                               | A | 04-11-1975          | JP 913350 C                | 21-07-1978          |
|   |   |                     | JP 52042432 B              | 24-10-1977          |

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number  
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(21) International Application Number: PCT/EP00/06057

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(25) Filing Language: English

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99114601.0 26 July 1999 (26.07.1999) EP

(71) Applicant (for all designated States except US): HUNTS-  
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(72) Inventor; and

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(74) Agents: MOENS, Marnix, Karel, Christiane et al.;  
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(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

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KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: POLYISOCYANATE COMPOSITIONS FOR FAST CURE

(57) Abstract: Use of a Titanium complex in a polyisocyanate composition comprising a titanium complex consisting of titanium and an acetoacetate ester in which the molar ratio of Ti to acetoacetate ester is in the range 1:2 to 1:8 and said acetoacetate ester is an ester of an alcohol containing 1 to 4 carbon atoms for accelerating the binding of lignocellulosic materials.

WO 01/07498 A1



## POLYISOCYANATE COMPOSITIONS FOR FAST CURE

This invention relates to polyisocyanate compositions and, in particular, to polyisocyanate compositions containing certain organometallic compositions based on Group IVB metals and which utility in accelerating the binding of the lignocellulosic material used in the manufacture of waferboard (known extensively as oriented strand board), medium density fiberboard and particle board (also known as chipboard).

The use of organic polyisocyanates as binders for lignocellulosic material in the manufacture of sheets or moulded bodies such as waferboard, chipboard, fibreboard and plywood is well known. In a typical process the organic polyisocyanate, optionally in the form of a solution, dispersion or aqueous emulsion, is applied to the lignocellulosic material which is then subjected to heat and pressure.

It has now been surprisingly found that specific Titanium compositions enhance the cure rate of binders such as starch, isocyanates when used for binding lignocellulosic materials especially oriented strand board

Furthermore It has been surprisingly found that certain polyisocyanate compositions containing certain compounds of Group IVB metals and acetoacetate esters are very stable on prolonged storage and provide significant acceleration to the binding of lignocellulosic material used in the core layers of waferboard (known extensively as oriented strand board), medium density fiberboard and particleboard while maintaining excellent physical properties.

According to the invention, a polyisocyanate composition comprising a titanium composition in which the molar ratio of Ti to acetoacetate ester is in the range 1 : 2.0 to 1:8 and said acetoacetate ester is an ester of an alcohol containing 1 to 4 carbon atoms.



The titanium composition used in the polyisocyanate composition of the invention is described herein as a "complex". It is believed that some of the acetoacetate ester will be chemically bound to the metal (Ti) but some can be described as "free" ester. The exact proportions which are bound and free will depend partly upon the exact molar ratios present in the complex but it has been shown that the "free" ester does influence the properties, particularly the stability on storage, of the polyisocyanate composition as a binder for lignocellulosic materials. The use of the word "complex" does not imply that said complex is necessarily separately prepared before addition to a polyisocyanate to form the compositions of the invention. The complex can be formed by preparing the inventive composition using several alternative methods as described hereinafter.

The molar ratio of titanium to acetoacetate ester in the complex is in the range 1 : 2.0 to 1 : 8. Preferably, in the range of 1 : 2.0 to 1 : 6 and more preferably in the range 1 : 2.5 to 1 : 5. In agreement with conventional theories about the co-ordination chemistry of titanium, it is believed that two molecules of acetoacetate ester will be chemically bound to a titanium atom and the remainder will be "free".

The preferred acetoacetate ester for preparing the complex is ethyl acetoacetate. The complex can be prepared from more than one acetoacetate ester but preferably only one acetoacetate ester is present in the complex.

Typically, the complex of titanium is prepared from a titanium alkoxide having the general formula  $M(OR)_4$  in which M is Ti and R is a substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group. Preferably, R contains up to 6 carbon atoms and, more preferably, up to 4 carbon atoms. Generally, all four OR groups will be identical but alkoxides derived from a mixture of alcohols can be used and mixtures of alkoxides can be employed when more than one metal is present in the complex. Suitable alkoxides include tetramethoxytitanium, tetra-ethoxytitanium, tetra-isopropoxytitanium, tetra-n-

propoxytitanium, tetrabutoxytitanium, tetrakis(2-ethylhexoxy)titanium, tetrakis(2-ethoxyethoxy)-titanium.

Alternatively, the complex can be prepared from condensed alkoxides of titanium. These compounds can be represented by the general formula  $RO[M(OR)_2O]_xR$ , wherein M and R have the same meaning as discussed above and x is an integer. Generally, these condensed alkoxides consist of a mixture containing compounds of the above formula with x having a range of values. Preferably, x has an average value in the range 2 to 16 and, more preferably, in the range 2 to 8. A condensed alkoxide is usually prepared by the controlled addition of water to an alkoxide, followed by removal of alcohol which is displaced. Suitable condensed alkoxides include the compounds known as polybutyl titanate and polyisopropyl titanate. Complexes of condensed alkoxides can also be prepared by forming a complex of an acetoacetate ester with an alkoxide, adding water to the complex and removing any by-product alcohol.

Other titanium compounds, such as titanium tetrachloride or alkoxides which have been substituted with, for example, glycol or phosphorus substituents can be used as raw materials for the formation of the complex used in the invention.

The complex can be readily prepared by mixing, for example, an alkoxide or condensed alkoxide with an appropriate amount of acetoacetate ester. Alcohol from the alkoxide will be displaced by the acetoacetate ester and, preferably, the displaced alcohol is removed by, for example, distillation. In a preferred method, 2 moles of acetoacetate ester per atom of Ti are added to an alkoxide or condensed alkoxide and the displaced alcohol is removed by distillation. Any additional acetoacetate ester required is then added to the stripped product. This method is advantageous because it provides a consistent product of known stoichiometry. It is possible to add all the acetoacetate ester in one charge and subsequently remove all the displaced alcohol but some of the "free"

acetoacetate ester is usually accidentally removed during this process, leading to inconsistent products and contamination of the displaced alcohol.

Alternatively, a product containing, for example, 2 moles of acetoacetate ester per Ti can be prepared according to the method outlined above and this can be mixed with a polyisocyanate. Any additional acetoacetate ester required to produce the polyisocyanate composition of the invention can be added to the polyisocyanate before or after the titanium-compound has been added. Other methods of preparing the composition of the invention will be apparent to a person skilled in this art.

The amount of titanium complex present in the polyisocyanate composition of the invention is usually in the range 0.01 to 5 % by weight, based on the polyisocyanate and, preferably, the amount is in the range 0.03 to 1 %. More preferably, the amount of complex present is in the range 0.05 to 0.5 % by weight with respect to polyisocyanate.

Polyisocyanates for use in the composition of the present invention may be any organic polyisocyanate compound or mixture of organic polyisocyanate compounds, provided said compounds have at least 2 isocyanate groups. Organic polyisocyanates include diisocyanates, particularly aromatic diisocyanates, and isocyanates of higher functionality.

Examples of organic polyisocyanates which may be used in the composition of the present invention include aliphatic isocyanates such as hexamethylene diisocyanate; and aromatic isocyanates such as m- and p-phenylene diisocyanate, tolylene-2,4- and tolylene-2,6-diisocyanate, diphenyl- methane-4,4'-diisocyanate, chlorophenylene-2,4-diisocyanate, naphthylene- 1,5-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate- 3,3'-dimethyl-diphenyl, 3-methyldiphenylmethane-4,4'-diisocyanate and diphenyl ether diisocyanate; and cycloaliphatic diisocyanates such as cyclohexane-2,4- and -2,3-diisocyanate, 1-methylcyclohexyl-2,4- and -2,6-diisocyanate and mixtures thereof and bis-



(isocyanatocyclohexyl)methane and triisocyanates such as 2,4,6-triisocyanatotoluene and 2,4,4-triisocyanatodiphenylether.

Modified polyisocyanates containing isocyanurate, carbodiimide or uretonimine groups may be employed as well. Further blocked polyisocyanates, like the reaction product of a phenol or an oxime and a polyisocyanate, may be used, having a deblocking temperature below the temperature applied when using the polyisocyanate composition.

The organic polyisocyanate may also be an isocyanate-ended prepolymer made by reacting an excess of a diisocyanate or higher functionality polyisocyanate with a polyol.

Water-emulsifiable organic polyisocyanates like those described in UK patent no. 1 444 933, in European patent publication no. 516 361 and in PCT patent publication no. 91/03082 can also be used.

Mixtures of isocyanates may be used, for example a mixture of tolylene diisocyanate isomers such as the commercially available mixtures of 2,4- and 2,6-isomers and also the mixture of di- and higher polyisocyanates produced by phosgenation of aniline/formaldehyde condensates.

Such mixtures are well-known in the art and include the crude phosgenation products containing methylene bridged polyphenyl polyisocyanates, including diisocyanate, triisocyanate and higher polyisocyanates together with any phosgenation by-products.

Preferred isocyanates to be used in the present invention are those wherein the isocyanate is an aromatic diisocyanate or polyisocyanate of higher functionality such as a pure diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates containing diisocyanates, triisocyanates and higher functionality polyisocyanates.





Methylene bridged polyphenyl polyisocyanates are well known in the art. They are prepared by phosgenation of corresponding mixtures of polyamines obtained by condensation of aniline and formaldehyde. For convenience, polymeric mixtures of methylene bridged polyphenyl polyisocyanates containing diisocyanate, triisocyanate and higher functionality polyisocyanates are referred to hereinafter as polymeric MDI. Suitable polyisocyanates include SUPRASEC<sup>TM</sup> DNR, SUPRASEC<sup>TM</sup> 2185, RUBINATE<sup>TM</sup> M and RUBINATE<sup>TM</sup> 1840, all available from Imperial Chemical Industries.

Preferably the polyisocyanate is liquid at room temperature.

In order to further improve the storage stability of the polyisocyanate composition of the present invention a diluent may be added to the composition. Suitable diluents include plasticizers of the type mentioned in "Taschenbuch der Kunststoff-Additive", Ed. by R. Gachter and H. Muller, Carl Hanser Verlag Munchen, third edition, 1989. Preferred diluents are phthalates, aliphatic carboxylates, fatty acid esters, linseed oil and soybean oil. These diluents are added in amounts of from 1 to 40 parts by weight per 100 parts by weight of polyisocyanate and preferably in amounts of from 1 to 15 parts by weight per 100 parts by weight of polyisocyanate.

The composition further may also comprise conventional additives like flame retardants, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, surfactants, thixotropic agents and other binders like formaldehyde condensate adhesive resins and lignin (optionally in combination with a lignin solvent such as described in PCT Patent Application No. EP96/00924).

The polyisocyanate composition of the present invention can be made by simply mixing the ingredients at room temperature.



The present invention is also concerned with a process for preparing lignocellulosic bodies by bringing lignocellulosic parts into contact with the present polyisocyanate composition and by pressing this combination.

Therefore the present invention also provides a process for binding lignocellulosic material comprising the steps of

- a) bringing said lignocellulosic material in contact with the present polyisocyanate composition and
- b) subsequently allowing said material to bind.

The lignocellulosic bodies are prepared by bringing the lignocellulosic parts into contact with the polyisocyanate composition by means such as mixing, spraying and/or spreading the composition with/onto the lignocellulosic parts and by pressing the combination of the polyisocyanate composition and the lignocellulosic parts, preferably by hot-pressing, normally at 140° C to 270°C and 2 to 6 MPa specific pressure.

Such binding processes are commonly known in the art.

In waferboard manufacture the lignocellulosic material and the polyisocyanate composition may be conveniently mixed by spraying the present polyisocyanate composition on the lignocellulosic material while it is being agitated.

The lignocellulosic material after treatment with the polyisocyanate composition is placed on caul plates made of aluminium or steel which serve to carry the furnish into the press where it is compressed to the desired extent usually at a temperature between 140° C and 270° C.

While the process is particularly suitable for the manufacture of waferboard known extensively as oriented strand board and will be largely used for such manufacture, the process may not be regarded as limited in this respect and can also be used in the



manufacture of medium density fiberboard, particle board (also known as chipboard) and plywood.

Thus the lignocellulosic material used can include wood strands, woodchips, wood fibres, shavings, veneers, wood wool, cork, bark, sawdust and like waste products of the wood working industry as well as other materials having a lignocellulosic basis such as paper, bagasse, straw, flax, sisal, hemp, rushes, reeds, rice hulls, husks, grass, nutshells and the like. Additionally, there may be mixed with the lignocellulosic materials other particulate or fibrous materials such as ground foam waste (for example, ground polyurethane foam waste), mineral fillers, glass fibre, mica, rubber, textile waste such as plastic fibres and fabrics.

When the polyisocyanate composition is applied to the lignocellulosic material, the weight ratio of polyisocyanate/lignocellulosic material will vary depending on the bulk density of the lignocellulosic material employed. Therefore, the polyisocyanate compositions may be applied in such amounts to give a weight ratio of polyisocyanate/lignocellulosic material in the range of 0.1 : 99.9 to 20 : 80 and preferably in the range of 0.5 : 99.5 to 10 : 90.

The polyisocyanate compositions of the present invention allows operating temperatures far below the standard operating temperatures. Hence major energy savings can be made.

If desired, other conventional binding agents, such as formaldehyde condensate adhesive resins, may be used in conjunction with the polyisocyanate composition.

More detailed descriptions of methods of manufacturing waferboard and similar products based on lignocellulosic material are available in the prior art. The techniques and equipment conventionally used can be adapted for use with the polyisocyanate compositions of the present invention.



The sheets and moulded bodies produced from the polyisocyanate compositions of the present invention have excellent mechanical properties and they may be used in any of the situations where such articles are customarily used.

5           The invention is illustrated but not limited by the following examples.

## EXAMPLE 1

A reactor was charged with tetraisopropyl titanate (1400kg, Tilcom® TIPT from ICI Vertec). Ethylacetoacetate (1282kg) was then added with stirring. The resulting product was a pale red liquid. The displaced alcohol (580 kg, isopropanol) was then removed by evaporation to leave a red liquid PRODUCT A (2090kg). This was then diluted by addition of ethylacetoacetate in the following molar ratio (1 mole PRODUCT A to 2.5M ethylacetoacetate) to yield PRODUCT B.

A polyisocyanate composition was then prepared comprising 0.18 parts weight of PRODUCT B described above and 100 parts by weight of standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) to yield a material PRODUCT C.

*Stability testing of PRODUCT C vs Standard Isocyanate (Comparative)*

The stability of PRODUCT C was evaluated by storing PRODUCT C 45° C and then testing the viscosity of each system at 25° C using a Brookfield viscometer at various time. The following data was obtained:

Results are reported below in Pa s.

| Days | PRODUCT C | Comparative |
|------|-----------|-------------|
| 21   | 280       | 244         |

To evaluate the utility of PRODUCT C in accelerating the curing of the core layers of an OSB panel against a standard polyisocyanate composition used industrially within the core of an OSB panel PRODUCT C was used to bind the softwood strands used in the core layers in the following manner:

*Panels containing Product C*

3 Layer boards were prepared of 15 x 400 x 400 mm at a density 650 kg/m<sup>3</sup>. MUPF resin was used to bind the face layers (11% resin loading based on dry wood). PRODUCT C was used to bind the core layer (4% resin loading based on dry wood). Both



layers also contained a sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The pre-pressing moisture content was 11 % in the face layers and 6% in the core layer.

5 *Standard Isocyanate (comparative)*

3 Layer boards were prepared of 15 x 400 x 400 mm at a density 650 kg/m<sup>3</sup>. MUPF resin was used to bind the face layers (11% resin loading based on dry wood) and standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) used to bind the core layer (4% resin loading based on dry wood). Both layers also  
10 contained a sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The pre-pressing moisture content was again 11 % in the face layers and 6% in the core layer.

To determine the minimum cycle time a press temperature of 190<sup>o</sup> C was used. The minimum possible cycle time was obtained by reducing the overall cycle time until a  
15 failure in panel performance was evident (either through a loss of control over panel thickness or through adhesive failure). The following results were obtained for panels prepared as described earlier:

|   | Standard Polyisocyanate | PRODUCT C |
|---|-------------------------|-----------|
| Minimum cook time<br>(seconds of pressing per mm<br>of panel thickness) | 7.0                     | 6.3       |

20

The composite produced under conditions described above were then tested using a range of industry standard tests to measure physical properties (Modulus of elasticity and rupture according to EN310 / V100 internal bond according to EN1087 / Swelling after 24hrs of soaking in water according to EN317). The measured properties showed no significant  
25 performance difference between composites prepared with SUPRASEC DNR and PRODUCT C and demonstrates the advantages of using polyisocyanate compositions of the invention to achieve accelerated binding of lignocellulosics relative to standard polyisocyanate compositions whilst not affecting physical performance of the resulting composite panels.



## EXAMPLE 2

A polyisocyanate composition was prepared comprising 0.18 parts by weight of PRODUCT B (described above) and 100 parts by weight of standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) to yield a material  
5 PRODUCT D.

To evaluate the utility of PRODUCT D in accelerating the curing of a OSB panel against a standard polyisocyanate composition used industrially within the core of an OSB panel PRODUCT D was then used to bind softwood strands in the following manner:

10 *Panels containing Product D*

3 Layer boards were prepared of 25 x 250 x 250 mm at a density 650 kg/m<sup>3</sup>. Standard polyisocyanate resin (SUPRASEC DNR, available from Imperial Chemical Industries) was used to bind the face layers (4% resin loading based on dry wood). PRODUCT D was used to bind the core layer (4% resin loading based on dry wood). Both  
15 layers also contained a sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The prepressing moisture content was 11 % in the face layers and 6% in the core layer.

*Standard Isocyanate*

20 3 Layer boards were prepared of 25 x 250 x 250 mm at a density 650 kg/m<sup>3</sup>. Standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) resin was used to bind the face layers (4% resin loading based on dry wood) and standard polyisocyanate (SUPRASEC DNR, available from Imperial Chemical Industries) used to bind the core layer (4% resin loading based on dry wood). Both layers also contained a  
25 sizing wax emulsion (SPG 60 available from Condea Chemie) at 1 % loading (solid wax) based on dry wood. The prepressing moisture content was again 11 % in the face layers and 6% in the core layer.

To determine the minimum cycle time a press temperature of 190° C was used. The minimum possible cycle time was obtained by reducing the overall cycle time until a  
30 failure in panel performance was evident (either through a loss of control over panel thickness or through adhesive failure). The following results were obtained for panels prepared as described earlier:

|   | Standard Polyisocyanate | PRODUCT D |
|---|-------------------------|-----------|
| Minimum cook time<br>(seconds of pressing per mm<br>of panel thickness) | 13.0                    | 11.0      |

The above clearly demonstrates the advantages of using polyisocyanate compositions of the invention to achieve accelerated binding of lignocellulosics relative to standard polyisocyanate compositions whilst not affecting physical performance of the resulting composite panels.





## CLAIMS

1. A polyisocyanate composition comprising a titanium complex consisting of titanium and an acetoacetate ester in which the molar ratio of Ti to acetoacetate ester is in the range 1: 2 to 1:8 and said acetoacetate ester is an ester of an alcohol containing 1 to 4 carbon atoms.
2. A polyisocyanate composition according to claim 1 in which the complex is a complex of titanium having a molar ratio of Ti to acetoacetate ester in the range 1 : 2 to 1 : 6.
3. A polyisocyanate composition according to claim 2 in which the molar ratio of Ti to acetoacetate ester is in the range 1 : 2.5 to 1 : 5.
4. A polyisocyanate composition according to any one of the preceeding claims in which the acetoacetate ester is ethyl acetoacetate.
5. A polyisocyanate composition according to any one of the preceding claims in which the complex has been prepared from a titanium alkoxide having the general formula  $M(OR)_4$  in which M is Ti and R is a substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.
6. A polyisocyanate composition according to claim 5 in which R contains up to 6 carbon atoms.
7. A polyisocyanate composition according to claim 6 in which R contains up to 4 carbon atoms.
8. A polyisocyanate composition according to any one of claims 1 to 7 in which the complex has been prepared from a condensed titanium alkoxide having the general formula  $RO[M(OR)_2O]_xR$  in which M is Ti and x is an integer and R is a substituted or unsubstituted, cyclic or linear, alkyl, alkenyl group.



9. A polyisocyanate composition according to claim 8 in which the average value of x is in the range 2 to 16.
10. A polyisocyanate composition according to any one of the preceding claims in which the complex is prepared from an alkoxide or condensed alkoxide and displaced alcohol is removed.
11. A polyisocyanate composition according to any one of the preceding claims in which the complex is present in an amount in the range 0.03 to 1 % by weight based on the polyisocyanate.
12. A polyisocyanate composition according to claim 11 in which the amount of complex is in the range 0.05 to 0.5 % by weight based on the polyisocyanate.
13. A polyisocyanate composition according to any one of the preceding claims in which the polyisocyanate is diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates.
14. A polyisocyanate composition according to any one of the preceding claims additionally comprising a diluent.
15. A polyisocyanate composition according to claim 14 in which the diluent is a phthalate, an aliphatic carboxylate, a fatty acid ester, linseed oil or soybean oil.
16. A polyisocyanate composition according to claim 15 in which the diluent is present in an amount in the range 1 to 40 parts by weight per 100 parts by weight of polyisocyanate.
17. A polyisocyanate composition according to any one of the preceding claims additionally comprising a formaldehyde condensate adhesive resin.
18. A polyisocyanate composition according to claim 17 in which the formaldehyde condensate adhesive resin is present in an amount in the range 1 to 40 parts by weight per 100 parts by weight of polyisocyanate.



19. A polyisocyanate composition according to claim 18 in which the formaldehyde condensate adhesive resin is present in an amount in the range 1 to 20 parts by weight per 100 parts by weight of polyisocyanate.
20. A process for binding lignocellulosic material comprising the steps of
- 5 a) bringing lignocellulosic material into contact with a polyisocyanate composition according to any one of the preceding claims and
- b) subsequently allowing said material to bind.
21. A process according to claim 20 in which the polyisocyanate composition is brought into contact with the lignocellulosic material and the combination thereby formed is
- 10 hot-pressed between metal plates at a temperature in the range 140° C to 270° C and a specific pressure in the range 2 to 6 MPa.
22. A process according to claim 20 or 21 in which the polyisocyanate composition is applied in such an amount as to give a weight ratio of polyisocyanate to lignocellulosic material in the range 0.1 : 99.9 to 20 : 80.
- 15 23. Use of a Titanium complex as defined in claim 1 for accelerating the binding of lignocellulosic materials.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06057

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/22 C08G18/76

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EP0-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.       |
|------------|--|-----------------------------|
| X          | WO 97 17388 A (ICI PLC)<br>15 May 1997 (1997-05-15)<br><br>claims 1,4,5,15,32-35,39,43,44; example 2   | 1,2,5-7,<br>10-16,<br>20-23 |
| A          | US 5 902 835 A (KIMOCK MICHAEL JOHN ET AL) 11 May 1999 (1999-05-11)<br>column 2, line 52 -column 3, line 14;<br>claims 1,2   | 1,4-10,<br>13               |
| A          | DATABASE WPI<br>Section Ch, Week 197746<br>Derwent Publications Ltd., London, GB;<br>Class A21, AN 1977-82339Y<br>XP002115290<br>& JP 50 138097 A (HITACHI LTD),<br>4 November 1975 (1975-11-04)<br>abstract | 1,5-7,<br>11,13             |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06057

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s)  | Publication<br>date  |
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